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Evaluation of the feasibility of preparing a reference material: active charcoal tubes charged with benzene, toluene and m-xylene

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Summary. Volatile organic compounds in air are mostly determined after enrichment by adsorption on active charcoal. A batch of three hundred active charcoal tubes was charged with benzene, toluene and m-xylene by drawing a volume of air with known composition through the tubes in such a manner as to charge each tube of the batch with exactly the same amounts. From this batch every tenth tube was analyzed gas-chromatographically. Further 60 charged tubes were stored under different conditions and analyzed within one year. It appeared that the charging was homogeneous and that no significant alteration was found within one year.

1 Introduction

Quality assurance becomes more and more essential in analytical work. The control of compliance of legislative limit values in the field of health, safety and environment presupposes reliable values. For quality control, reference materials get a paramount role [1, 2]. They are applicable for calibration of equipment, achievement of traceability of calibration, improvement of measurement quality, verification of accuracy of results and daily quality controls.

For workplace air monitoring usually a known volume of air is sucked through an adsorption tube to collect the organic vapours. Active charcoal is successfully used for the sampling of a large number of hazardous organic compounds, e.g. aromatic hydrocarbons [3–10]. In the laboratory, the collected components are desorbed by solvents and analyzed gas-chromatographically. For the determination of the desorption efficiency e.g. the phase equilibrium method is practicable and easy to handle. But for the determination of the collection efficiencies, and above all, for the complete validation of a method gaseous standards are required. Most laboratories are not equipped for this type of calibration. Using reference material can be an alternative way.

With a dynamically generated test gas it is possible to charge a large number of adsorption tubes with defined amounts of volatile organic compounds. Such kinds of tubes, e.g. charged with definite amounts of benzene, toluene and m-xylene, are usable as a reference material for single laboratory controls or for interlaboratory comparisons.

There are different methods for generating test gases [11–17]. The test gas generation following the saturation vapour pressure principle has the advantage that gases are generated from each liquid and solid substance with definite vapour pressure while the concentration of the working substance in the pure carrier gas is independently variable in the range of the TLV-values. As the test gas is produced dynamically with a fast equilibrium adjustment, wall adsorption effects have no influence. The chosen concentration is stable over weeks.

2 Description

2.1 Test gas generation

For benzene, a carcinogenic compound with a German TLV-value of 16 mg/m^3, a smaller concentration was chosen than for toluene (TLV-value: 380 mg/m^3) or m-xylene (TLV: 440 mg/m^3). Figure 1 shows the principle of the test gas equipment [18–20].

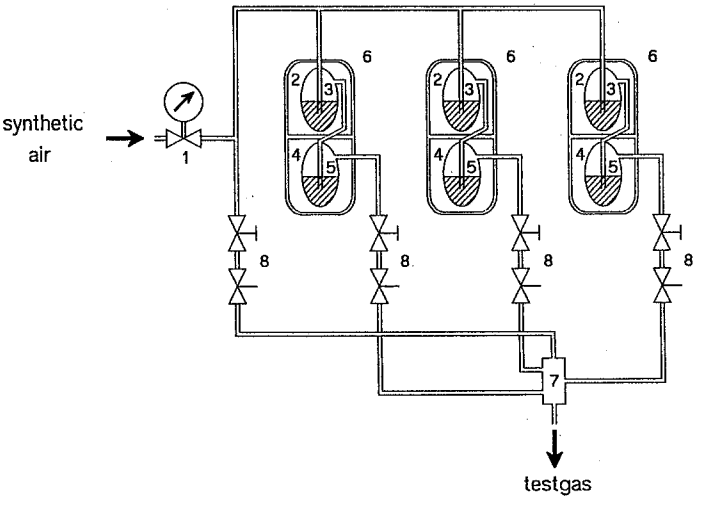

Fig. 1. Three component test gas equipment. *1* pressure regulator; *2* thermostate for the enriching flask; *3* enriching flask; *4* cooling thermostate; *5* condenser; *6* vacuum jacket; *7* mixing chamber; *8* needle-/shut off-valve combination

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Synthetic air (20/21 vol% O_2 in N_2) was used as carrier gas. After pressure regulation, the inlet gas stream was split into two channels. Through the first channel the carrier gas was split into three enriching flask-condenser containers, filled with benzene, toluene or m-xylene. Control of the gas streams was achieved by three needle-/shut off-valve combinations. The enrichment of the carrier gas with the hazardous compound occurred in the temperable enriching flasks. After this the gas reached the condensers, whose temperatures were about 20 K below the temperature of the enriching flasks. So the gas was supersaturated and the surplus of the compound was condensed or frozen out. The flows of all three enriching flask-condenser containers were combined, and with the second channel, the saturated gas stream could be diluted with pure carrier gas. The dilution ratio was variable by a further needle-/shut off-valve combination. The inlet pressure was adjusted at 1 bar, regulated by a needle valve and controlled by a precision manometer (pressure regulator) to obtain a gas pressure high enough for the correct function of the equipment.

2.2 Reliability determinations

The concentration of each component was calculated and then exactly determined gravimetrically. For this purpose, adsorption tubes with 800 mg active charcoal were conditioned by drawing an inert gas stream of approx. 1 l/min for 5 min through each one. Each tube was charged with only one component by closing the other shut-off valves during 6–18 h and then the collected amount was determined by weighing.

The homogeneity of the multi-component test gas mixture was controlled in parallel by an automatically working gas chromatograph with a gas sample loop of 0.150 ml. During the whole charging the test gas flows through the sample loop which injects an aliquot periodically every 7 min and analyzes it to control and to document the homogeneity. The injected gas volume was very small related to the total volume of test gas passing the sample loop in 7 min. So the total amount of the adsorbed components was nearly unchanged.

With the above mentioned equipment (see Fig. 1), a batch of 300 charcoal tubes type NIOSH was charged. These tubes (Dräger Co.) had a length of 7 cm and an inner diameter of 4 mm and were filled with 150 mg of charcoal separated by a piece of urethane foam in a front section with 100 mg and a back section with 50 mg charcoal. The final flow of the test gas station had been adjusted at 25 ml/min, the concentration: 0.0333 mg/l benzene, 0.333 mg/l toluene and 0.233 mg/l m-xylene. Each tube was loaded for 10 min under these conditions. Then, the tubes were closed with polypropylene caps.

The homogeneity of the charged tubes was controlled by analyzing every tenth of it by head-space gas chromatography.

3 Results

3.1 Results for the homogeneity of the test gas

The resulting serial chromatograms of the three component test gas showed a good homogeneity of the mixture. The relatively standard deviation was better than 2%.

3.2 Results for the homogeneity of the charging

A standard solution of benzene, toluene and m-xylene in benzyl alcohol was made with a concentration equal to the one in the desorbed samples. Ten uncharged tubes were opened and the charcoal of each was filled into a vial. 2 ml standard solution were added. These samples were shaken for 4 h and then analyzed by means of head-space gas chromatography.

30 charged tubes were desorbed with 2 ml benzyl alcohol each and analyzed in the same way.

The standard deviations are shown in Table 1. These values show a good homogeneity of the charging (and desorption).

3.3 Results for the stability during storage

The stability of the charged tubes was investigated, too. Sixty charged charcoal tubes were selected at random and stored under three different conditions:

- in a refrigerator at 2° C in the dark,
- at a non-sunlit place in a climated laboratory room at 20° C and
- in the dark in a box above a drying kiln with a constant temperature of 40° C.

The stored tubes were analyzed after 30 days, 90 days, half a year and after one year (see Table 2).

The loaded tubes turned out to be stable over at least 12 months, independent of storage conditions. No negative slope versus time was found.

Table 1. Relative standard deviations for benzene (10 µg), toluene (100 µg) and m-xylene (70 µg)

Samples	Relative standard deviation [%]		
	Benzene	Toluene	m-Xylene
Standard with charcoal	1.8	1.7	1.9
Charged tubes	2.2	2.3	2.7

Table 2. Recovery rates for stored charged tubes

Storage		Recovery rates [%]		
[Days]	[° C]	Benzene	Toluene	m-Xylene
30	2	99.1	100.6	101.8
	20	99.4	99.7	102.0
	40	100.5	98.7	101.0
90	2	99.0	99.3	99.1
	20	103.1	100.0	100.3
	40	99.7	100.3	100.7
180	2	99.1	98.9	98.4
	20	99.7	100.1	101.3
	40	100.3	98.4	99.0
360	2		103.5	102.5
	20	99.6	102.3	101.3
	40	96.0	100.4	100.1

4 Conclusion

It was possible to show that active charcoal tubes can be charged homogeneously by this method and that the charged tubes do not show any loss of substance within one year. So, the evaluation of the feasibility of preparing a reference material was successful.

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